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Rupert E.v.H. Spence, Stephen L. Buchwald, and John F. Richardson

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Department of Chemistry
Massachusetts Institute of Technology
77 Massachusetts Avenue
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Attempts to convert 2,2'-cyclobuta-1,1'-dimethylzirconacyclopentadiene into the corresponding bismole by treatment with phenylbismuth dibromide, led instead to the formation of 1,5-Bis(cyclobuta)-3,4,7,8-tetramethylcyclooctatetraene. A preliminary mechanistic study of this unusual transformation was also carried out.

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Author responsible for correspondance and proofs: Prof. Stephen L. Buchwald, Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA.

The Unexpected Formation of 1,5-Bis(cyclobuta)-3,4,7,8-tetramethylcyclooctatetraene from a Zirconacyclopentadiene.

Rupert E. v. H. Spence and Stephen L. Buchwald*

Department of Chemistry
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139, USA

John F. Richardson[a]

Department of Chemistry
University of Louisville
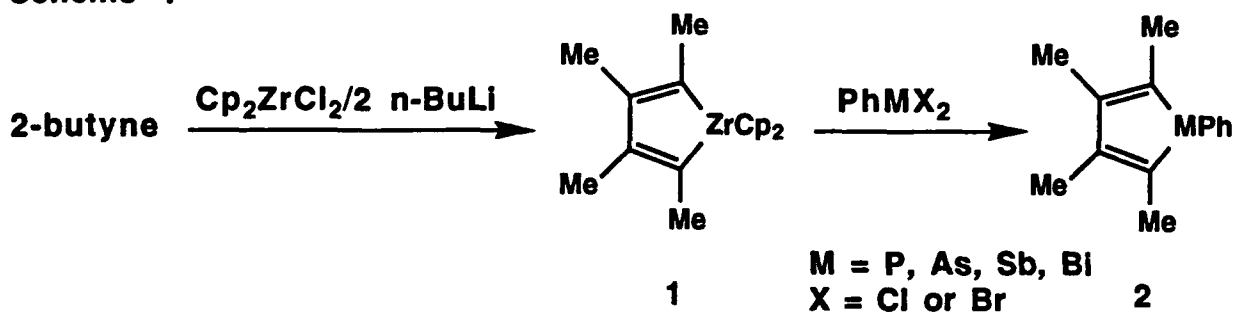Louisville, Kentucky 40292, USA

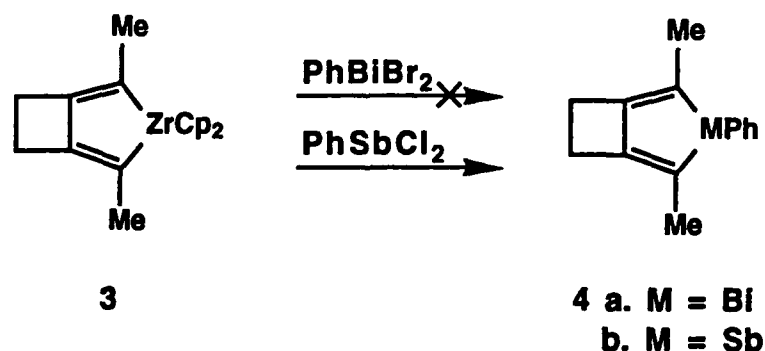Dedicated to Professor Salo Gronowitz on the occasion of his 65th birthday.

[a]Author to whom questions regarding crystallography should be addressed.

The conversion of readily prepared zirconacyclopentadienes[1] to the corresponding main group heterocycles by the Fagan-Nugent method has been shown to be extremely versatile.[2,3] For example, reaction of zirconacycle 1 (prepared by the sequential addition of 2 equivalents n-BuLi and 2-butyne to zirconocene dichloride)[1e] with phenylpnictogen dihalides gives the respective main group heterocycles 2 in high isolated yields (Scheme 1).[2] During the course of our study on the synthesis of antimony and bismuth heterocycles,[3] we were therefore surprised to find that treatment of phenylbismuth dibromide with an equivalent of zirconacycle 3[1d] failed to give the desired phenylbismole 4a (Scheme 2). Instead, cyclooctatetraene 5[4] was produced (Scheme 3). In contrast, in previous work from our laboratory, only the expected phenylstibole 4b was obtained upon treatment of 3 with $PhSbCl_2$ (Scheme 2).[5,6]

Scheme 1

$$2\text{-butyne} \xrightarrow{\text{Cp}_2\text{ZrCl}_2/2 \text{ n-BuLi}} \mathbf{1} \xrightarrow{\text{PhMX}_2} \mathbf{2}$$

M = P, As, Sb, Bi
X = Cl or Br

Scheme 2

$$\mathbf{3} \xrightarrow[\text{PhSbCl}_2]{\text{PhBiBr}_2 \times} \mathbf{4}$$

4 a. M = Bi
   b. M = Sb

Scheme 3

$$\mathbf{3} \xrightarrow{\text{PhBiBr}_2} \mathbf{5}$$
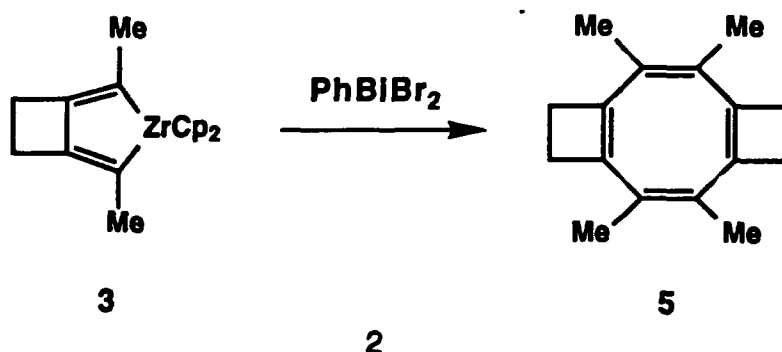
2

Cyclooctatetraene **5** can be isolated in 83% yield as a bright yellow crystalline solid from the addition of **3** to $PhBiBr_2$. The ^1H NMR spectrum of the crude reaction mixture indicates that **5** is the major organic product and that the by-products of the reaction include Cp_2ZrBr_2, Ph_3Bi and Ph_2BiBr and other unidentified zirconocene species. A black precipitate also forms which we believe to be elemental bismuth.

In order to fully characterize compound **5**, its X-ray structure was determined. A view of the molecule is shown in Figure 1 and selected bond lengths and angles are given in Table 2. The molecule adopts a tub conformation and, in general, the bond lengths and angles are similar to those found in other cyclooctatetraene structures.[7] Interestingly, the double bonds of the cyclooctatetraene ring are found to be endocyclic to the fused four membered rings (similar to related cyclooctatetraene structures),[7g,h] while in the precusor zirconacycle **3**[1d] the double bonds are found exocyclic to the cyclobutane ring. The torsion angle of 49° defined by C(2)-C(1)-C(8)-C(7) is less than that found in the parent cyclooctatetraene (55°),[7a] octamethylcyclooctatetraene (68°)[7c,d] and other cyclooctetraene structures.[7c,i,j] This flattening of the molecule, relative to the parent compound, is most likely due to the cyclobutene rings (perflurotetracyclobuta-1,3,5,7-cyclooctetraene, with four fused cyclobutene rings, is planar).[7g,8,9] Consistent with this solid state flattening, the solution ring inversion barrier of **5** is found to be 10 ± 0.2 Kcal/mol (coalesance occurs at -67 °C in THF-d_6 as determined by variable temperature ^1H NMR) significantly less than that observed for the parent cyclooctatetraene (13.7 Kcal/mol)[10a] and tetramethylcyclooctatetraene (23 Kcal/mol).[10b]

Bismole **4a** has been prepared from the dilithio salt **6** (Scheme 4) and is found to be stable both in solution and the solid state.[11] However, addition of $PhBiBr_2$ to **4a** cleanly gives cyclooctatetraene **5**. Importantly, slow addition of $PhBiBr_2$ (1 equivalent) to an excess of zirconacycle **3** (4 equivalents) in benzene gives significant amounts of bismole **4a** together with compound **5** and unreacted **3**. Consequently, we believe that addition of zirconacycle **3** to $PhBiBr_2$ leads to the formation of bismole **4a**, but subsequent reaction with $PhBiBr_2$ gives cyclooctatetraene **5**.

Interestingly, treatment of **3** with $BiBr_3$, $SbCl_3$ and $GaCl_3$ also gives **5** as the major organic product, as determined by ^1H NMR. Furthermore, when benzene solutions of bibismole **7** (Scheme 5), prepared from the reductive coupling of **4b**,[11] are stored at room temperature for 48 h, compound **5** forms in >90% yield and elemental bismuth precipitates. It is therefore apparent that there is some thermodynamic preference for the formation of cyclooctatetraene **5**.

Scheme 4

6 → PhBlBr₂ → **4b** → PhBlBr₂ → **5**
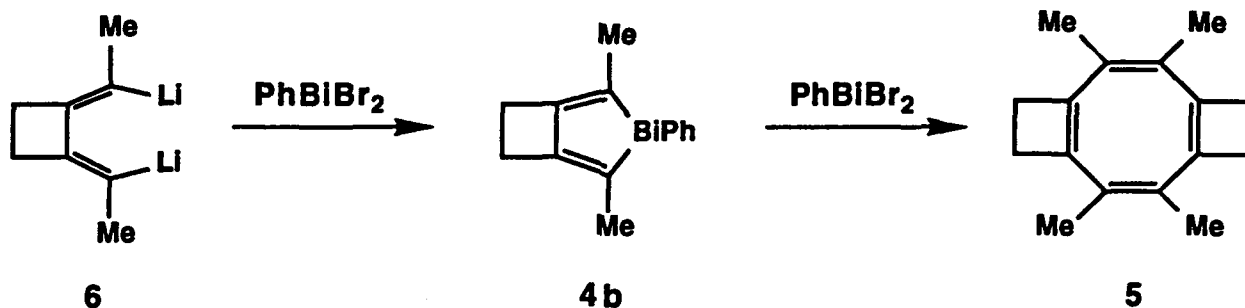
Scheme 5

7 → 48 h / benzene → **5**
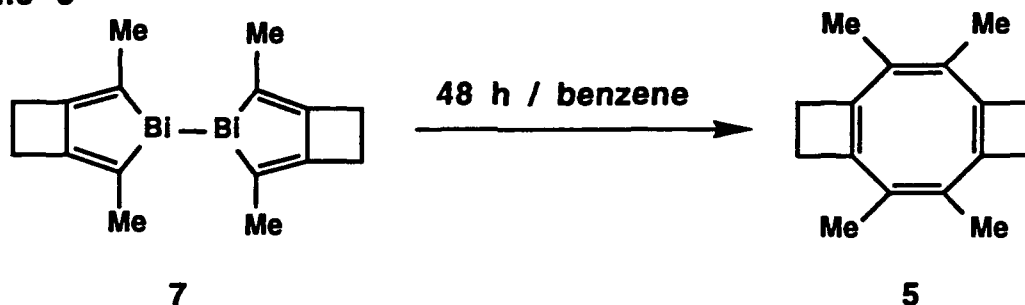
Attempts to convert other pnictoles or zirconacycles to the corresponding cyclooctatetraenes have, to date, been unsuccessful. Interestingly, we have found that introduction of a cyclobutane ring into the 3,4 position of zirconacyclopentadienes can promote the formal oxidation of the zirconium bound carbon fragment.[12] For example, zirconacyclopentadiene **8** upon treatment with PhSbCl₂ and PhBiBr₂ cleanly reverts to 1,6-bis(trimethylsilyl)hexa-1,5-diyne, **9**, the initial organic precursor to **8** (Scheme 6). Clearly, the differing steric and electronic effects of the trimethylsilyl groups relative to methyl groups leads to alternative products for **3** and **8**.

Scheme 6
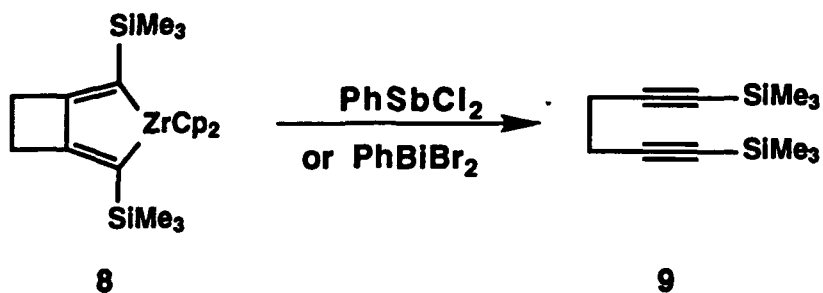
8 → PhSbCl₂ or PhBiBr₂ → **9**

Experimental

Preparation of 1,5-Bis(cyclobuta)-3,4,7,8-tetramethylcyclooctatetraene, **5.** To a suspension of phenylbismuth dibromide (446 mg, 1 mmol) in benzene (15 mL) was added a solution of zirconacycle 3^{1d} (327 mg, 1 mmol; C_6H_6 15 mL), under argon. The reaction quickly darkened and on stirring overnight a yellow solution with black ppt formed. The benzene was removed *in vacuo*, diethyl ether was added and the solution then passed through a column of neutral alumina. Subsequent chromatography (silica column/hexane elutant) removed the Ph_3Bi by-product and gave pure **5**, which can be recrystallised from hexane at -80 °C.

Yield, 88 mg, 83 %. Mp 131-132 °C. Anal. $C_{16}H_{20}$: C 90.51; H 9.49.

MS [IP 70 ev; m/e (% rel. int.)]: 212 (91, M), 197 (73), 183 (77), 182 (75), 169 (100), 167 (80).

^1H (300 MHz, C_6D_6, 25 °C): δ 2.30 (8H, s), 1.53 (12H, s).

^1H (500 MHz, d^8-THF, -100 °C): δ 2.25 (4H, d, 10.7 Hz), 2.15 (4H, d, 10.7 Hz), 1.53 (12H, s).

$^{13}C\{^1H\}$ (300MHz, C_6D_6, 25 °C): δ 144.3, 131.4, 26.6, 16.4.

X-Ray Diffraction Analysis: A crystal of **5** with dimensions of 0.12 x 0.24 x 0.27 mm^3 was mounted on a glass fiber. An Enraf-Nonius CAD-4 diffractometer using Mo-Kα radiation (λ = 0.71073 Å) was used to measure the unit cell dimensions and to collect data. Unit-cell constants were obtained from least squares refinement, using the setting angles of 25 accurately centered reflections in the range 15°<θ<18°. Crystal data were determined to be: a = 12.588(2) Å; b = 7.843(1) Å; c = 13.804(2) Å; β = 108.98(2)°; V = 1288.3 $Å^3$; Z = 4; M = 212.34 amu; D_x = 1.09 g cm^{-3}; F(000) = 464; μ = 0.6 cm^{-1}. The space group was determined to be $P2_1/n$ (alternate no. 14) from systematic absences.

The data were collected at 23(2) °C using the ω-2θ scan technique (scan width = 0.8 + 0.34tanθ). The scan rate was varied from 1 to 3 ° min^{-1}(in θ) and data were collected to a maximum 2θ of 50°. A total of 2379 reflections were collected, of which

2269 were unique; 1399 with $I>3\sigma(I_o)$ were included in structural analysis. As a check on crystal stability three standard reflections were monitored every 60 min. and showed a decay of 6%; decay corrections ranged from 1.00 to 1.03. Lorentz and polarisation corrections were applied to the data but no absorption correction was made. A secondary extinction correction was applied $(5.4(5) \times 10^{-7})$.[13]

The structure was solved by direct methods (MULTAN80).[14] A total of 8 carbon atoms were located from an E-map and the remaining atoms were located from a series of difference Fourier maps. Hydrogen atoms were located and their positions refined with isotropic thermal parameters fixed at $1.3B_{eq}$ of the bonded C atom. The structure was refined in full-matrix least-squares where the function minimized was $\Sigma w(|F_o| - |F_c|)^2$ and the weight was defined as $w = [\sigma(F)^2 + (0.005F)^2 + 0.3]^{-1}$.[15] Scattering factors were taken from Cromer and Waber[16] and anomalous dispersion effects were included in F_c.[17] The final cycle of refinement included 206 parameters and converged (largest parameter shift was 0.1 times its esd) with $R = \Sigma||F_o| - |F_c||/\Sigma F_o = 0.046$, $R_w = [\Sigma w(F_o - F_c)^2/\Sigma w F_o^2]^{1/2} = 0.043$ and $S = 1.13$. The final difference electron density map showed maximum and minimum values of 0.18 (3) and -0.18 (3) $e\text{\AA}^{-3}$.

The atomic parameters are presented in Table 1. Selected bond lengths and angles are given in Table 2 and a view of the molecule is shown in Figure 1. Anisotropic thermal parameters, H parameters and structure factor tables are available upon request.

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17. D. T. Cromer, *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4 Table 2.3.1.

Table 1: Table of Positional Parameters and Their Estimated Standard Deviations.

Atom	x	y	z	Beq ($\mathring{A}^2$)[a]
C1	0.4870(2)	0.3155(3)	0.6263(2)	3.29(6)
C2	0.4715(2)	0.4649(3)	0.6669(2)	3.30(5)
C3	0.3845(2)	0.5420(3)	0.7030(2)	3.34(6)
C4	0.2758(2)	0.5397(3)	0.6471(2)	3.43(5)
C5	0.2345(2)	0.4568(3)	0.5460(2)	3.30(6)
C6	0.2494(2)	0.3061(3)	0.5063(2)	3.44(6)
C7	0.3154(2)	0.1508(4)	0.5430(2)	3.60(6)
C8	0.4243(2)	0.1547(3)	0.5984(2)	3.44(5)
C9	0.6029(2)	0.3620(4)	0.6235(2)	4.28(7)
C10	0.5856(2)	0.5349(4)	0.6710(2)	4.44(7)
C11	0.4289(2)	0.6270(4)	0.8057(2)	5.03(7)
C12	0.1858(2)	0.6241(4)	0.6797(2)	5.28(7)
C13	0.1460(2)	0.5169(4)	0.4478(2)	4.54(7)
C14	0.1630(2)	0.3421(4)	0.4025(2)	4.86(7)
C15	0.2509(3)	-0.0123(4)	0.5092(2)	5.66(8)
C16	0.4938(3)	-0.0034(4)	0.6333(2)	4.95(7)
H9A	0.664(2)	0.290(3)	0.670(2)	5.5*
H9B	0.612(2)	0.369(3)	0.553(2)	5.5*

[a]*Beq* is defined as $(4/3) \cdot [a^2\beta_{11} + b^2\beta_{22} + ...ab(\cos\gamma)\beta_{12} + ...]$

9

Table 2. Table of Selected Bond Lengths (Å) and Angles (°) for Compound **5**.

C(1)-C(2)	1.340 (4)	C(5)-C(6)	1.341 (4)
C(1)-C(8)	1.471 (4)	C(5)-C(13)	1.523 (3)
C(1)-C(9)	1.517 (4)	C(6)-C(7)	1.469 (4)
C(2)-C(3)	1.473 (4)	C(6)-C(14)	1.518 (3)
C(2)-C(10)	1.522 (4)	C(7)-C(8)	1.334 (3)
C(3)-C(4)	1.334 (3)	C(7)-C(15)	1.505 (4)
C(3)-C(11)	1.501 (4)	C(8)-C(16)	1.504 (4)
C(4)-C(5)	1.473 (3)	C(9)-C(10)	1.552 (4)
C(4)-C(12)	1.501 (4)	C(13)-C(14)	1.551 (5)

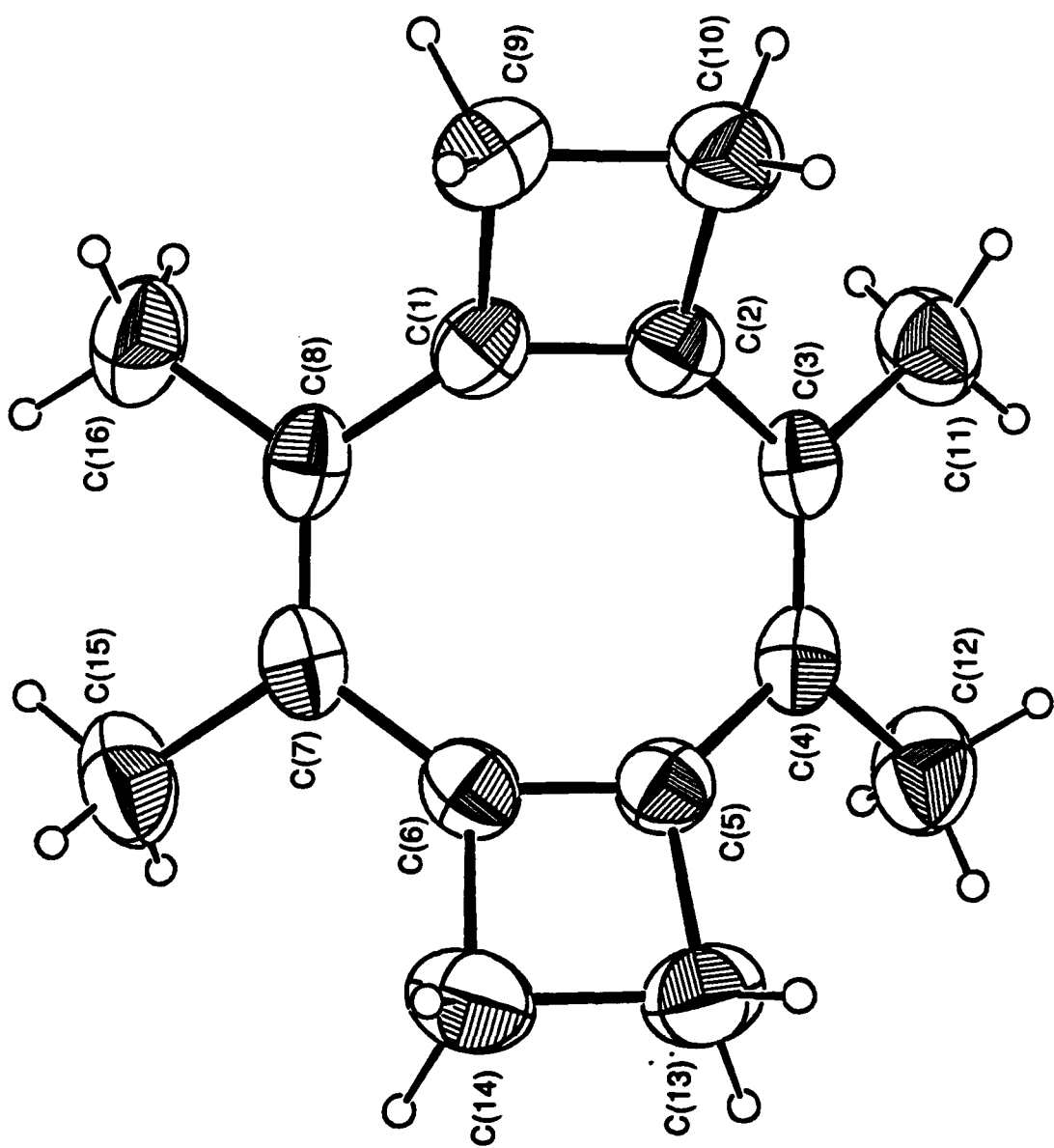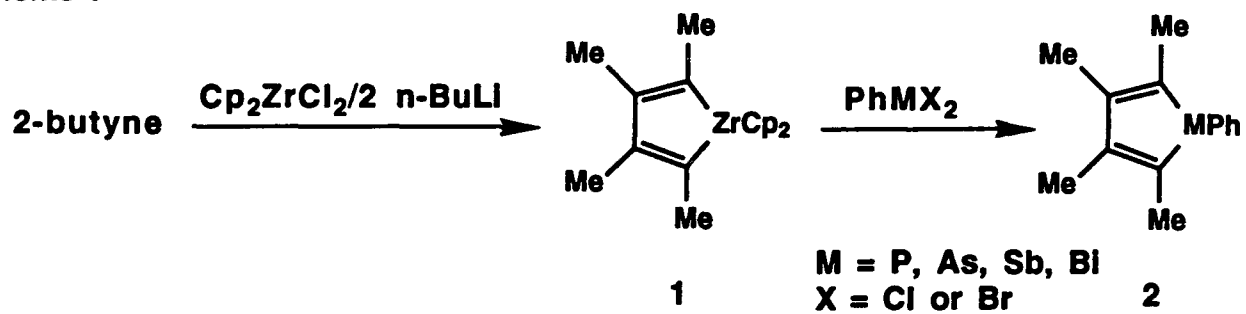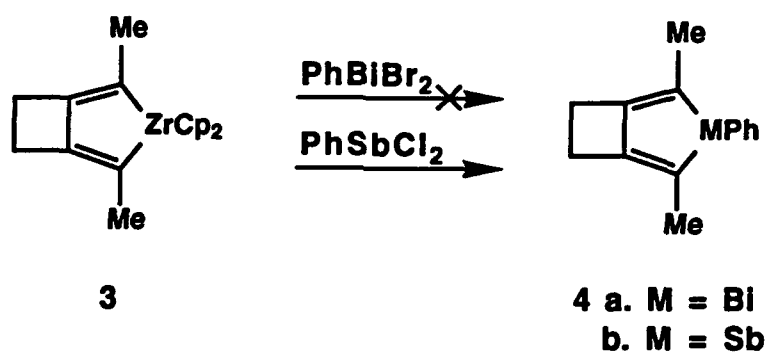|			
C(2)-C(1)-C(8)	136.1 (3)	C(6)-C(5)-C(13)	93.9 (2)
C(2)-C(1)-C(9)	94.1 (2)	C(5)-C(6)-C(7)	136.8 (2)
C(8)-C(1)-C(9)	129.7 (2)	C(5)-C(6)-C(14)	94.0 (2)
C(1)-C(2)-C(3)	136.6 (2)	C(7)-C(6)-C(14)	129.1 (2)
C(1)-C(2)-C(10)	93.9 (2)	C(6)-C(7)-C(8)	122.6 (2)
C(3)-C(2)-C(10)	129.5 (2)	C(6)-C(7)-C(15)	114.2 (2)
C(2)-C(3)-C(4)	122.3 (2)	C(8)-C(7)-C(15)	123.1 (2)
C(2)-C(3)-C(11)	114.4 (2)	C(1)-C(8)-C(7)	122.2 (2)
C(4)-C(3)-C(11)	123.3 (3)	C(1)-C(8)-C(16)	114.6 (2)
C(3)-C(4)-C(5)	122.2 (2)	C(7)-C(8)-C(16)	123.1 (2)
C(3)-C(4)-C(12)	123.5 (2)	C(1)-C(9)-C(10)	86.0 (2)
C(5)-C(4)-C(12)	114.2 (2)	C(2)-C(10)-C(9)	85.9 (2)
C(4)-C(5)-C(6)	136.3 (2)	C(5)-C(13)-C(14)	85.9 (2)
C(4)-C(5)-C(13)	129.6 (2)	C(6)-C(14)-C(13)	86.2 (2)

Figure 1: Crystallographic View of **5**.

Figure 1. Some Blackwell and Richardson

Scheme 1

2-butyne $\xrightarrow{\text{Cp}_2\text{ZrCl}_2/2\ n\text{-BuLi}}$ **1** $\xrightarrow{\text{PhMX}_2}$ **2**

M = P, As, Sb, Bi
X = Cl or Br

Scheme 2

3 $\xrightarrow[\text{PhSbCl}_2]{\text{PhBiBr}_2 \times}$ **4 a. M = Bi**
  b. M = Sb

Scheme 3

3 $\xrightarrow{\text{PhBiBr}_2}$ **5**

Scheme 4

| 6 | 4 b | 5 |

Scheme 5

48 h / benzene

| 7 | 5 |

Scheme 6

PhSbCl$_2$
or PhBiBr$_2$

| 8 | 9 |